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THE 1,2-FLUORINE ATOM MIGRATION IN THE EPOXIDE OF 1,1-DICHLORODIFLUOROETHENE. THE INFRARED SPECTRUM OF DICHLOROFLUOROACETYL FLUORIDE

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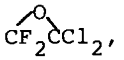
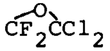
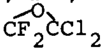
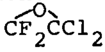
Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata. Sucursal 4, Casilla de Correo 16, (1900) La Plata (Argentina)

SUMMARY

The epoxide of 1,1-dichlorodifluoroethene,  $\overset{O}{CF_2CCl_2}$, and chlorodifluoroacetyl chloride, $CF_2ClC(O)Cl$, were the principal products of the gas-phase thermal reaction of NO_2 with 1,1-dichlorodifluoroethene, CF_2CCl_2, in presence of O_2 at 257.3 K and 300.2°K. Five other products: COF_2, $COCl_2$, $O_2NCF_2C(O)Cl$, $CF_2ClCCl_2NO_2$ and $CF_2ClCCl_2O_2NO_2$ were also formed in minor amounts or traces, depending on the relation between NO_2, CF_2CCl_2 and O_2. The initial pressure of NO_2 was varied between 0.7 and 4.7 torr, that of CF_2CCl_2 between 18.4 and 81.9 torr, and that of O_2 between 50.4 and 696.3 torr. The isomerization of  $\overset{O}{CF_2CCl_2}$ to $CF_2ClC(O)Cl$ was never observed, but, in the presence of mercury vapour, the rearrangement of  $\overset{O}{CF_2CCl_2}$ to $CFCl_2C(O)F$ occurred, involving the unexpected 1,2-migration of a fluorine atom. The infrared spectrum of $CFCl_2C(O)F$ is given. The elementary reactions sequence is proposed to explain the formation of $CF_2ClC(O)Cl$ and  $\overset{O}{CF_2CCl_2}$.

RESULTS AND DISCUSSION

The gas-phase thermal reaction system formed by NO_2, 1,1-dichlorodifluoroethene, CF_2CCl_2, and O_2 was studied at 257.3

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and 300.2 K. The initial pressure of NO_2 was varied between 0.7 and 4.7 torr, that of CF_2CCl_2 between 18.4 and 81.9 torr and that of O_2 between 50.4 and 696.3 torr [1].

For analyzing the reaction mixture from each experiment, the reaction vessel was cooled down to liquid air temperature, O_2 pumped out, and the remaining condensate separated in fractions by vacuum distillations. The infrared spectra of every fraction were recorded on Perkin-Elmer 325 spectrometer, using 10 cm gas cell with sodium chloride windows. Seven products were identified by their infrared bands: COF_2 [2] in the fraction I volatile at 153 K, $COCl_2$ [3], $CF_2ClC(O)Cl$ [4] and $\overset{\diagup O \diagdown}{CF_2CCl_2}$ [5] in the fraction II volatile at 183 K and $O_2NCF_2C(O)Cl$ [6], $CF_2ClCCl_2NO_2$ and $CF_2ClCCl_2O_2NO_2$ in the fraction III remaining as residue. The infrared identification of $CF_2ClCCl_2NO_2$ was made comparing the respective spectra of CF_2ClNO_2 [7] and CF_2ClCCl_3 [8], and that of $CF_2ClCCl_2O_2NO_2$ was done by its bands at 1300 and 1758 cm^{-1}, characteristic to the peroxynitrate group [9,10], and whose intensities decreased as a function of time because of the decomposition of $CF_2ClCCl_2O_2NO_2$. The principal products were $CF_2ClC(O)Cl$ and $\overset{\diagup O \diagdown}{CF_2CCl_2}$, the others appearing in minor amounts or traces and their distribution depended on the relation between NO_2, CF_2CCl_2 and O_2.

Both $CF_2ClC(O)Cl$ and $\overset{\diagup O \diagdown}{CF_2CCl_2}$ were stable at room temperature. In the consecutive infrared spectra of their mixture, the respective bands intensities remained constant during 6 days. After adding air with atmospheric moisture to this mixture no change was observed after 5 days.

In one of the runs, the vapour of the mercury from the boiler of the diffusion pump was carried accidentally by atmospheric air into the reaction vessel, due to a failure in the condensation system. Notwithstanding, the experiment was allowed to continue until the total consumption of CF_2CCl_2, and the separation into fractions had been completed. In the infrared spectrum of the fraction II of this run, the bands of $\overset{\diagup O \diagdown}{CF_2CCl_2}$ were not observed, instead those of other compound appeared, with a band at 1878 cm^{-1} indicating the presence of the C(O)F group. The bands of $CF_2ClC(O)Cl$ remained unaltered. Several chromatograms of this fraction II were recorded on a Gow-Mac gas chromatograph, provided with a gas density balance and using a 5% SE-30 on CG column at 245 K, with N_2 as carrier gas. Two peaks appeared in each chromatogram, one of which corresponded to $CF_2ClC(O)Cl$. As the density balance chromatograph can be used to determine the molecular weight of an unknown compound [11], the following formula was derived for this case: $M_x = [KA_x + f_xPVM_c]/f_xPV$, where P and V are the pressure and volume of a gaseous mixture, K the chromatograph constant determined for pure CF_3OF, A_x the peak area of the compound X, f_x its molar fraction and M_x and M_c the respective molecular weights of X and the carrier gas. The value of 145±8 was obtained for M_x, which, in addition to the infrared band at 1878 cm^{-1} indicating the C(O)F group, suggested that the compound X was $CFCl_2C(O)F$, whose theoretical molecular weight is 149. The spectrum corresponding to $CFCl_2C(O)F$, obtained by the subtraction of the bands of $CF_2ClC(O)Cl$ from the infrared spectrum of the mixture of the both compounds, is illustrated in Fig. 1. The

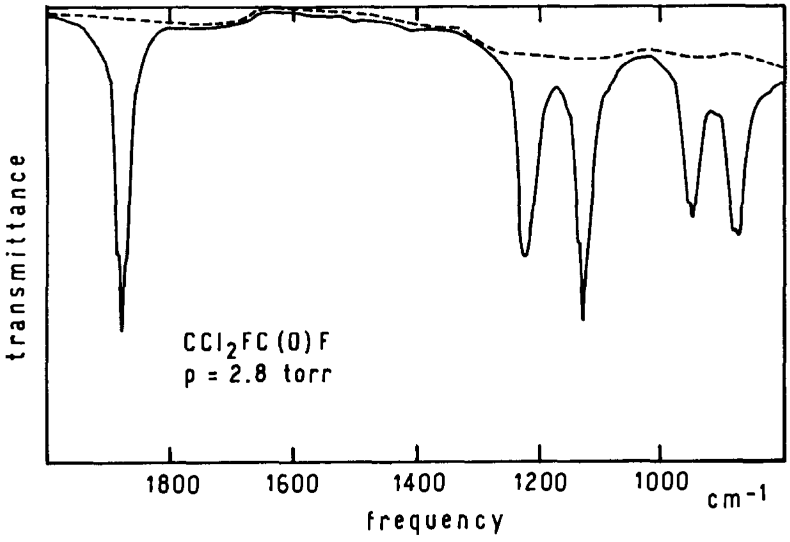

Fig. 1. The infrared spectrum of $CFCl_2C(O)F$.

pressure of $CFCl_2C(O)F$ was derived subtracting that of $CF_2ClC(O)Cl$ from the pressure of the mixture. The amount of the $CF_2ClC(O)Cl$ was determined using infrared calibration curve allowing to convert the absorption intensities at 1818 cm^{-1} to the pressures of $CF_2ClC(O)Cl$. This curve was constructed in previous work [12], combining gas chromatography with infrared spectroscopy.

The comparison of the respective spectra of $CFCl_2C(O)F$ and $\overbrace{CF_2CCl_2}^{O}$ is presented in the Table I.

TABLE I

The comparison of the infrared spectra of gaseous $CFCl_2C(O)F$ and $\overbrace{CF_2CCl_2}^{O}$

$CFCl_2C(O)F$ Frequency cm^{-1} [a]	$\overbrace{CF_2CCl_2}^{O}$ Frequency cm^{-1} [a]	Tentative Assignment
1878 (vvs)		C=O str.
	1500 (vvs)	$\overbrace{C-C}^{O}$
1223 (vs) 1125 (vvs)	1249 (vs) 1099 (s)	C-F
955 (s) 947 (s)	958 (vvs) 936 (vs)	C-C
880 (s) 867 (s)	717 (s) 713 (s)	C-Cl

[a] v = very, s = strong.

In order to confirm the reproducibility of the conversion observed, various experiments were carried out in the presence of mercury vapour and atmospheric air, trying to reproduce the conditions of the run when the unexpected isomerization occurred. Several consecutive spectra were recorded for each final reaction mixture of these experiments to characterize the temporal behavior of the products. Here, the progressive decrease of the epoxide band intensities at 1500 cm^{-1} was observed simultaneously with the increase of the band intensities of $CFCl_2C(O)F$ at 1878 cm^{-1}.

The formation of $CFCl_2C(O)F$ starting from $\overbrace{CF_2CCl_2}^{O}$ indicated that 1,2-fluorine atom migration is involved in the rearrangement. Similar migrations were reported for two radicals: $CF_2Cl\dot{C}FCl$ giving $CF_3\dot{C}Cl_2$ in the presence of amines with low ionization potential [13], and $CH_2F\dot{C}F_2$ giving $CF_3\dot{C}H_2$ in the presence of hydrogen atoms generated by mercury photosensitized decomposition of hydrogen [14].

As the 1,2-migration of chlorine atoms does not occur, the formation of $CF_2ClC(O)Cl$ and $\overbrace{CF_2CCl_2}^{O}$ is explained by the following reactions sequence, where $R' = O_2NCF_2CCl_2$, $R'' = CF_2ClCCl_2$ and R' or $R'' = R$, : $NO_2 + CF_2CCl_2 \rightarrow R'$, $R' + O_2 + M \rightarrow R'O_2 + M$, $2\ R'O_2 \rightarrow 2\ R'O + O_2$, $R'O \rightarrow O_2NCF_2C(O)Cl + Cl$, $Cl + CF_2CCl_2 \rightarrow R''$, $R'' + O_2 + M \rightarrow R''O_2 + M$, $2\ R''O_2 \rightarrow 2\ R''O + O_2$, $R''O \rightarrow \underline{CF_2ClC(O)Cl} +$ Cl, $RO_2 + CF_2CCl_2 \rightarrow RO + \underline{\overbrace{CF_2CCl_2}^{O}}$

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